

High-Pressure, High-Temperature Hydrogen Permeability Measurements of Supported Thin-Film Palladium Membranes

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Abstract

Interest in enhancing hydrogen recovery from water-gas shift reactors and reformers has motivated the development of hydrogen permeable membranes. High hydrogen flux, robustness, low cost and high selectivity are desirable characteristics for membrane materials. Palladium has excellent surface catalytic activity, reasonably high permeability, and some alloys are reputed to be resistant to sulfur-poisoning. Although palladium is expensive and lacks mechanical toughness, membranes composed of thin Pd films supported on robust substrates are viable candidates for commercial application. Substrates include hydrogen-permeable dense metal or a porous metal that would not significantly diminish hydrogen flux.

In this study, the hydrogen permeation of palladium-coated membranes was determined at temperatures between 623-1173 K and pressures up to 2.75 MPa. Thin-films of palladium were coated on tantalum and porous stainless steel (5.0- μm pore size). The thickness of the palladium on bulk tantalum ranged from 0.025- μm (sputter-coated) to 2- μm (electroless deposition), while the thickness on the porous stainless steel was approximately 20- μm . The hydrogen flux obtained with the Pd on porous stainless steel membrane was 17 times greater than that of a bulk palladium membrane (1-mm thick) and 10 times greater than the Pd-coated Ta membrane.

Introduction

Viable membrane candidates have been identified with compositions ranging from metals, ceramics, and polymers to any combination thereof. Although many compositions and methods have been proposed for hydrogen separation membranes, palladium has been a consistently popular material in most of the viable hydrogen membrane concepts, especially at temperatures above the range associated with polymeric membranes.

Palladium was initially identified as having an affinity for hydrogen in the mid-1800's [1-3], and since has been a material involved in extensive hydrogen transport research at primarily low to moderate temperatures and pressures. Palladium has been a preferred membrane material because of its reasonably high permeability and catalytic surface, which is thought to rapidly dissociate molecular hydrogen. However, due to its high cost

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and poor mechanical characteristics (i.e. α - β -phase transition) [4], research has focused on methods of reducing the amount of palladium needed (i.e. Pd-coated substrates), decreasing the effect of hydrogen embrittlement (i.e. Pd alloys), and/or eliminating palladium as a membrane component (i.e. porous membranes).

Attempts to reduce the amount of palladium used in membrane development have focused primarily on coated substrates. Utilizing thin films of palladium (0.1 to 100 μm) can provide the advantageous surface characteristics of bulk palladium, without the high cost and poor mechanical characteristics. However, for this technology to succeed, the substrate must exhibit a lower overall hydrogen transport resistance than the palladium. Thus, a successful composite membrane may be achieved by the application of a thin palladium coating to a dense, highly permeable metal, such as tantalum or a porous substrate, such as porous stainless steel.

Except for the work of Makrides [5], direct experimental measurements of the hydrogen permeability in tantalum are rare. It is expected that the calculated permeability would be difficult to attain in a real system due to the dominance of surface effects on the tantalum. Unlike palladium, surface oxidation and the lack of significant catalytic activity typically inhibits the absorption and/or dissociation of hydrogen molecules on tantalum surfaces.

To remedy the problem of tantalum's unfavorable surface effect, composite materials have been developed in which tantalum is coated with a thin layer (1 to 10- μm) of palladium. Such composites are of interest because they would seem to be economically viable, catalytically active, and mechanically durable candidates as membrane materials for hydrogen separation and membrane reactor applications. Palladium-coated tantalum membranes of this type have been demonstrated as hydrogen separation devices in disk [6], tubular [6,7] and foil [8,9] form. Of the aforementioned studies, two of them [8,9] were done using thin tantalum foils (10-40- μm). Although the results were quite promising, they cannot be considered indicative of the behavior of bulk tantalum. The two remaining studies of palladium-coated tantalum membranes did employ bulk materials (>0.5-mm thick) at low-to-moderate pressure (20-373 kPa) [6,7]. The permeability of the tantalum membranes under these conditions was less than predicted for bulk Ta [10]. This lower permeability was attributed to transport resistances in the Pd layer, the Pd-Ta interface and in the gas phase-Pd boundary. There was a very slight increase in permeability with increasing temperature. The temperature range examined in one study [6] was relatively narrow and the increase in permeability was minor, therefore the investigators did not draw any conclusions from this trend.

Expressions for Hydrogen Flux and Permeability

Detailed derivations of the governing equations for hydrogen transport through dense membranes are described elsewhere [11,12], however a generalized description is given here.

Hydrogen transport through the membrane can be described by "flux", which is defined as the rate of hydrogen passing through the membrane per unit area. Assuming that the

rate-limiting step in the hydrogen transport mechanism is diffusion and that transport is uni-directional, the hydrogen flux can be described by Equation 1.

$$N_{H_2} = -k \frac{(P_{H_2,ret}^{0.5} - P_{H_2,perm}^{0.5})}{X_M} \quad (1)$$

Where N_{H_2} is the hydrogen flux, k is the membrane permeability, X_M is the membrane thickness and $P_{H_2,Ret}$ and $P_{H_2,Per}$ are the partial pressure of hydrogen on the retentate and permeate sides of the membrane, respectively. It should be noted that flux is inversely proportional to membrane thickness. Therefore in order to increase flux as thin a membrane as possible is desired. However, the mechanical integrity must also be maintained and a minimal thickness is required to maintain mechanical integrity, depending on the physical conditions to which the membrane will be subjected.

In the absence of experimental permeability results, the permeability can be estimated from the product of solubility and diffusion constant data.

Experimental

Bulk Palladium and Tantalum Membrane Preparation

Palladium and tantalum membranes were fabricated by punching 19-mm diameter disks out of 1-mm thick sheets (Alfa Aesar, at least 99.999% pure). The palladium disks were polished using 800 grit silicon carbide paper prior to mounting into Inconel 600-alloy holders using a welding technique developed at the National Energy Technology Laboratory (NETL). The mounted membrane, in its holder, was welded to predetermined lengths of 19-mm O.D. Inconel 600 tubing on both sides of the membrane holder assembly. These tubes acted as “extension tubes” and served to contain pressure and house components carrying feed gas and permeate gas both to and from the membrane. The mounting configuration is illustrated in Figure 1.

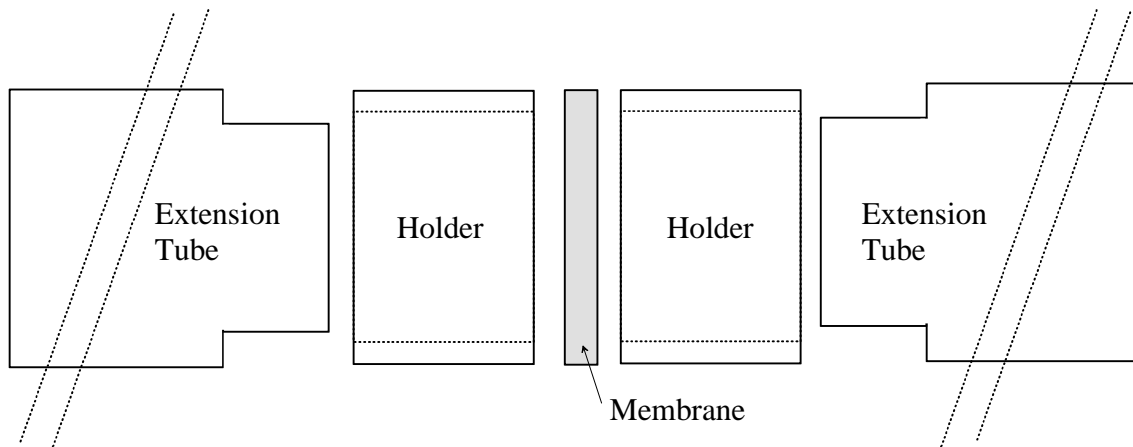


Figure 1: Schematic of the Membrane set-up.

After welding into the holders, the tantalum membranes were etched using an acid mixture of 20 vol-% HNO₃, 20 vol-% HF, and 60 vol-% H₂SO₄ and rinsed with distilled water in order to remove surface oxides and contaminants before testing and/or coating.

Palladium Coated Tantalum Membrane Preparation

Palladium coated tantalum membranes were prepared by either electroless plating or cold plasma sputter coating. Electroless plating was done at REB Research using a deposition technique developed by Buxbaum and described in a series of published results [6,7,13,14]. In this procedure, the surface of the tantalum was roughened and cleaned of oxides and oil using abrasives and detergent solutions. The tantalum surface was electrolytically hydrided with the noble metal serving as the cathode. Electroless plating was used to apply an approximately 1-2- μ m thick palladium film to the tantalum surface, using hydrazine as the reducing agent rather than hypophosphate, as reported in literature. The plated metal was heated to enhance the adhesion of the palladium coating.

Cold plasma sputter-coating was done at the National Energy Technology Laboratory (NETL) using a Denton Vacuum Desk II TSC cold plasma-discharge sputter equipped with a palladium target (Alfa Aesar, 99.9% pure). Before sputtering, all surfaces except those to be coated were masked. In a typical coating procedure, the mounted membrane substrate(s) were argon etched for 60 seconds to remove any physisorbed contaminants, and sputtered with palladium in cycles of 999 seconds until the desired coating thickness, either 0.04 or 1.2- μ m, was obtained. The process was repeated to coat the second side of the disk. The 0.04- μ m thickness was verified by performing an X-ray photoelectron spectroscopy (XPS) depth profile. The 1.2- μ m coating was verified by calculation based on weight increase and by scanning electron microscopic measurement of the membrane cross section. For the 0.04- μ m coating, XPS indicated that the maximum palladium thickness was in the center of the membrane with a decrease in thickness approaching the edge, probably due to a shadowing effect of the holder walls blocking palladium deposition near the edges. This trend was expected to hold for the 1.2- μ m coating, but was not measured.

Palladium Coated Stainless Steel Membrane Preparation

The Pd on porous stainless steel membranes were prepared by Professor Y. H. (Ed) Ma of Worcester Polytechnic Institute (WPI) [15]. The porous substrate, a 6.35-mm OD, 316L porous stainless steel tube with a mean pore diameter of 5- μ m, was obtained from Mott Corporation. The porous substrate was then coated on the outside with approximately 20- μ m of palladium via an electroless plating method. Fabrication and initial (low pressure) testing was done at WPI before shipping of the membrane to NETL.

Once at NETL, the Pd on porous stainless steel membranes were mounted by TIG welding 6.35-mm OD stainless steel tubing to each side of the membrane tube. The membrane was then placed within 19-mm OD Inconel Alloy 600 tubing to allow the counter current flow system desired (see Figure 1).

NETL Hydrogen Membrane Testing Unit

The hydrogen membrane testing (HMT) unit at NETL [5-7] was designed and constructed to allow testing of hydrogen separation membranes at high temperatures and pressures, up to 1173 K, and 3.1 MPa, respectively. A simplified schematic of the HMT unit is illustrated elsewhere [11,12,16].

The membrane unit feed gas consisted of a mixture of 10 percent helium in hydrogen. Helium was used to detect membrane leaks. Since helium does not have the ability to permeate palladium, its detection in the permeate stream would indicate a leak in the membrane or membrane-to-holder seal. The hydrogen-helium feed stream flow was controlled from 190 to 250 sccm. An argon sweep gas was passed over the permeate side of the membrane at a rate that maintained the concentration of hydrogen in the permeate at less than 6.0 mol-%. The hydrogen-containing permeate stream was directed to a Hewlett Packard 5890 Series II gas chromatograph equipped with a packed zeolite column and thermal conductivity detector for hydrogen quantification.

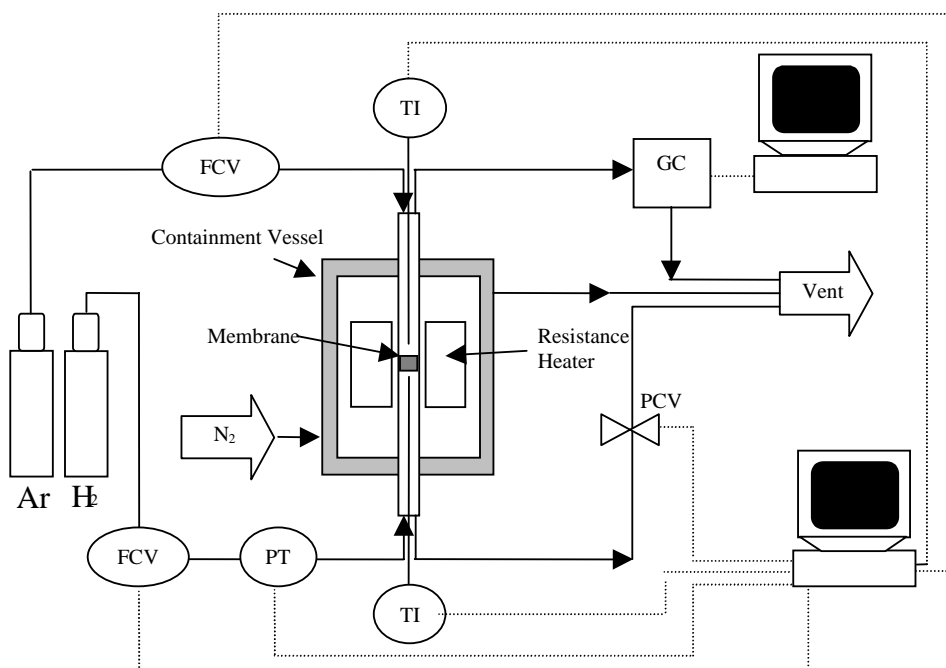


Figure 2. Schematic of Hydrogen Membrane Test Unit.

Results and Discussion

The permeability results along with literature values are summarized in Figure 3. Four separate bulk 1-mm thick palladium membranes were prepared and tested in order to insure repeatability in fabrication and testing. It should be noted that these are the first high-temperature, up to 1173 K, and high-pressure, up to 2.75 MPa, measurements of H₂ permeability in Pd. The permeability results for bulk palladium were consistent and closely match the literature values of Koffler, et al [17], despite the higher temperatures and pressures employed.

The permeability results for the Pd coated on porous stainless steel membranes were much less than predicted in the literature, almost 1/10 that of literature values. However some reduction in permeability is expected both due the blockage of some of the surface area by the porous stainless steel and because surface resistances become more prevalent with thinner membranes. That is, lower permeability is an inherent characteristic of thinner membranes due to the increasing significance of surface effects relative to diffusion. In addition, the permeability of these did not increase with temperature as expected. The membranes failed when tested above 750 K as evidenced by detection of helium in the permeate stream. Another possibility is that the lack of high temperature stability and the lack of higher permeability at higher temperatures may have been due to metal-metal interactions that may have yielded H_2 impermeable, mechanically unsound alloys, i.e. the Pd and stainless steel may have been diffusing into each other.

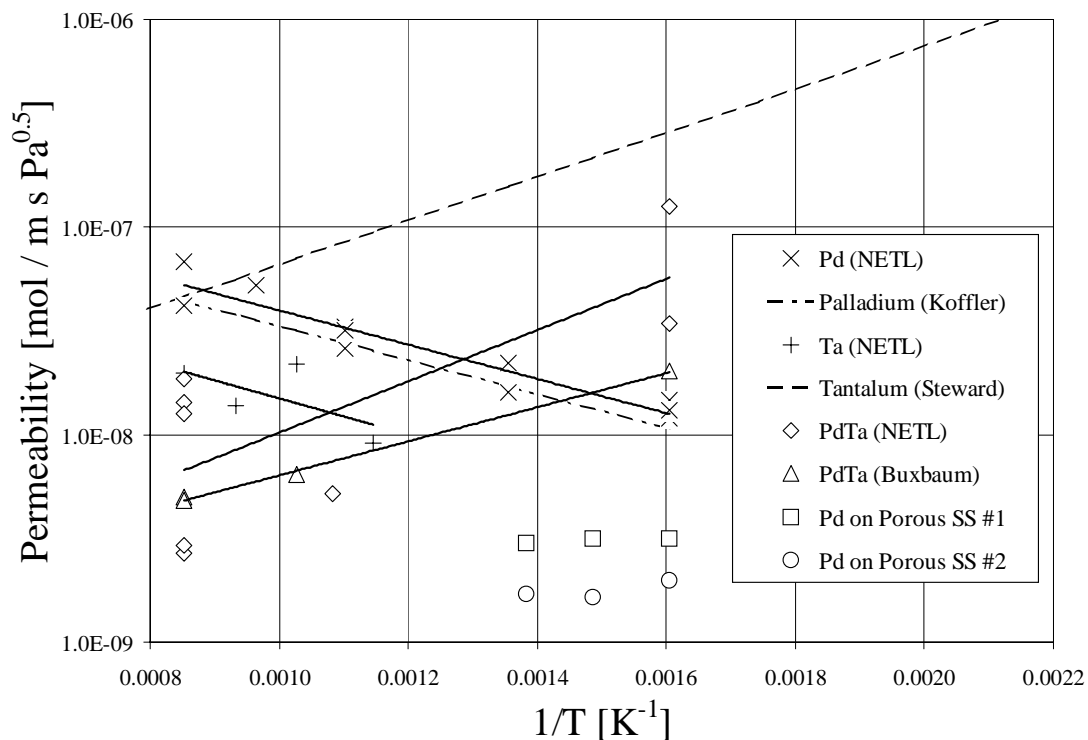


Figure 3. Permeability Results of tested Membranes and Literature Results

According to literature, the permeability of Ta decreases with increasing temperature (Figure 3). This is expected because prior low-pressure studies reveal that the decrease of H_2 solubility in Ta with increasing temperature [10] is more significant than the increase in diffusion coefficient. However, the bulk Ta tested at NETL showed the opposite trend with temperature.

The permeability results for the two bulk Ta membranes were scattered. Both the scatter and increase of permeability with temperature were probably caused by surface effects. Surface oxidation or contamination during testing probably caused the adsorption /

dissociation of H₂ on the surface to be the rate limiting step for H₂ diffusion through the Ta. And because of the direct temperature dependence on the adsorption / dissociation rate, the overall permeability was shown to increase with increasing temperature.

However, when 1-mm Ta membranes were coated with a thin layer of Pd, the expected permeability / temperature dependence of Ta resulted as shown by the PdTa (NETL) and PdTa (Buxbaum) permeability results. It appears as though the Pd coating “lends” its superior catalytic surface to the bulk Ta. This supports the hypothesis that negative surface effects with the bulk Ta may have been the rate-limiting step for H₂ diffusion.

It should also be noted that even with the Pd coating the permeability results for the Ta dominant membranes are much less than expected from a literature correlation. However, Steward’s correlation for Ta permeability was based on the product of low-pressure solubility and diffusivity data. Several sets of diffusion coefficient data [18-20] that were approximately 50% lower than the values used in the calculation were excluded [21]. With this in mind, one might conclude that the Pd coated on Ta data might provide fairly accurate Ta permeability data as long as the Pd does not have a significant effect on the overall rate of H₂ diffusion. Also our tests are high-pressure tests, and high partial pressure of H₂ increases the concentration of hydrogen in Ta and thereby decreases the diffusion constant of H₂ in Ta.

A simple model combining the individual rates for each layer can be used to determine if the Pd layers would have a significant effect on the overall permeability of a PdTa membrane. This is done by first assuming that the flux of hydrogen through each of the three layers of the membrane was equal.

Equation 1 was then used to derive an expression for the flux of each layer of the composite membrane. These three equations were rearranged to solve for the pressure gradient driving force in each layer and then added to yield an overall expression for the permeability of the membrane. Equation 2 presents this result in the form of the inverse permeability.

$$\frac{X_t}{K_t} = 2 \frac{X_{Pd}}{K_{Pd}} + \frac{X_{Ta}}{K_{Ta}} \quad (2)$$

This “theoretical” permeability for Pd-coated Ta membranes can then be calculated from the low-pressure literature correlations [17, 22] values for Pd and Ta and are shown in Figure 4. The two palladium layers of equal thickness deposited on both sides of a bulk tantalum disk are displayed with the thickness of both the Pd and Ta layers as Pd/Ta. A theoretical membrane with a 0.1-mm Pd and 1.0-mm Ta is presented along with the Buxbaum membrane dimensions (0.002/1). For the PdTa (0.1/1) membrane the predicted permeability values fall between both the bulk Pd and Ta values, showing that both materials have a significant effect on the overall predicted permeability values. However, for the PdTa (0.002/1) membrane the predicted permeability values are very close to the predicted values for Ta.

Therefore it is possible that permeability results of Ta thinly coated with Pd may be used to provide experimental permeability results for Ta. However, because of the significant scatter of the PdTa (NETL) results presented in this study, additional tests are required to provide accurate experimental Ta permeability measurements. But it should be noted that despite the scatter, our high-pressure permeability results for Pd coated Ta are much lower than that prior literature reports on low-pressure tantalum permeability [10]. This may be because the high partial pressure of H₂ decreases the diffusion coefficient of hydrogen in tantalum.

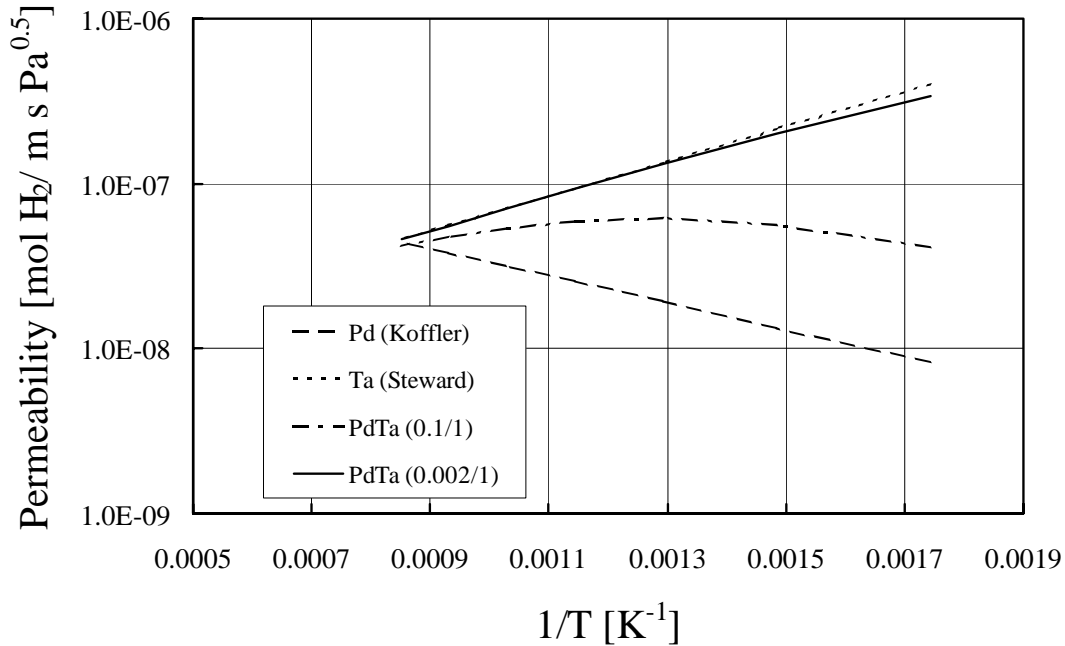


Figure 4. Permeability for Theoretical PdTa and Bulk Pd and Ta (Pd/Ta Thicknesses in mm).

It should be noted that if the thickness of a membrane is decreased the predicted flux increases (see Equation 1). In order to show the advantage of thinner membranes such as Pd on porous SS, the flux was plotted versus the reciprocal of temperature in Figure 5. In order to calculate the flux for each membrane/condition a H₂ pressure difference of 1 Pa^{0.5} was assumed. The resulting fluxes for the Pd on porous SS are much higher than the thicker bulk membranes.

By using a thin coating of Pd (~20-μm) and a porous substrate significant cost savings can be realized. In this case the porous stainless steel provides the mechanical strength for the membrane while significantly less (2% of the Pd need for a 1-mm thick Pd membrane) Pd is employed. Obviously some balance between mechanical properties, desired flux, and material cost will need to be considered. However, the supporting of membranes on porous substrates shows great potential.

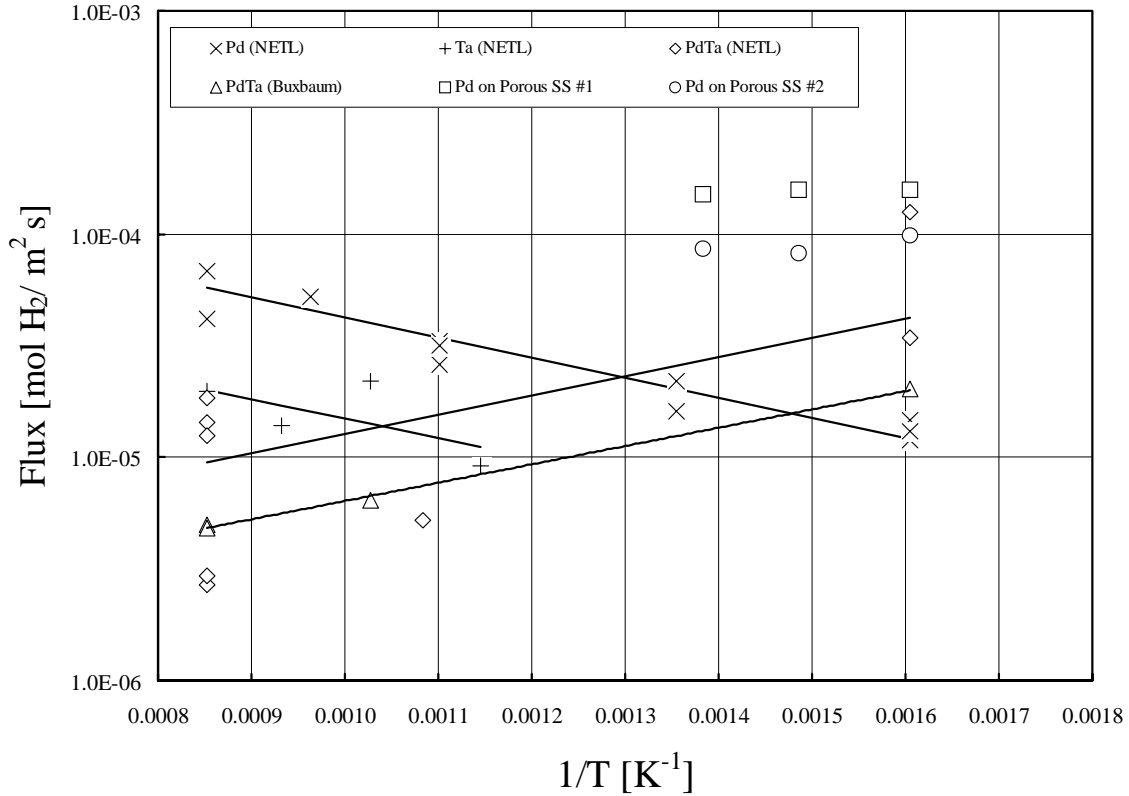


Figure 5. Flux Comparison of Tested Membranes

Conclusions

- The agreement between the experimental and literature Pd results verified our fabrication and testing procedures.
- Thin coatings of Pd were successfully applied to Ta membranes. The permeability results followed the expected temperature dependence of Ta. This supports the hypothesis that negative surface effects with the bulk Ta may have been the rate-limiting step for H₂ diffusion for bulk Ta. Also, it was demonstrated that Ta membranes with a very thin layer of Pd might be used to provide experimental Ta permeability results.
- It was shown that very high H₂ fluxes could be obtained with a thin layer of Pd supported on porous stainless steel.

Nomenclature

N_{H_2}	Hydrogen flux.
k	Membrane permeability constant.
$P_{H_2,Ret}$	Hydrogen partial pressure of the retentate or feed stream.
$P_{H_2,Per}$	Hydrogen partial pressure of the permeate or “product” stream.
X_M	Membrane thickness.

Disclaimer

Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

References

1. Deville, H. St.-C.; Troost, L.; Comptes rendus 57 (1863) 965.
2. Deville, H. St.-C.; Comptes Rendus 59 (1864) 102.
3. Graham, T.; Phil. Trans. Roy. Soc. 156 (1866) 399.
4. Grashoff, G.J.; Pilkington, C.E.; Corti, C.W.; "The Purification of Hydrogen – A Review of the Technology Emphasizing the Current Status of Palladium Membrane Diffusion," Platinum Metal Reviews 27 No. 4 (1983) 157-169.
5. Makrides, A.; Wright, M.; McNeill, R.; (1965) Final Report Contract DA-49-189-AMC-136(d); Tyco Lab, Waltham, MA.
6. Buxbaum, R.E.; Marker, T.L.; "Hydrogen Transport Through Non-Porous Membranes of Palladium-Coated Niobium, Tantalum and Vanadium," J. Membrane Sci. 85 (1993) 29-38.
7. Buxbaum, R.E.; Kinney, A.B.; "Hydrogen Transport Through Tubular Membranes of Palladium-Coated Tantalum and Niobium," Ind. Eng. Chem. Res. 35 (1996) 530-537.
8. Moss, T.S., Peachey, N.M., Snow, R.C., Dye, R.C., "Multilayer Metal Membranes for Hydrogen Separation," Intl. J. Hydrogen Energy, 23 (2) (1998) 99-106.
9. Peachey, N.M., Snow, R.C., Dye, R.C., "Composite Pd/Ta Membranes for Hydrogen Separation," J. Membrane Sci. 111 (1996) 123-133.
10. Veleckis, E. and Edwards, R. J. Phys. Chem. 73 (3) 1969, 683.
11. Morreale, B.D., M.V. Ciocco, R.M. Enick, B.I. Morsi, B.H. Howard, A.V. Cugini, K.S. Rothenberger, "The Permeability of Bulk Palladium at Elevated Temperatures and Pressures" J. of Mem. Sci. In Press 2002.
12. Morreale, B.D., Evaluation of Inorganic, Hydrogen Membranes at Elevated Temperatures and Pressures, M.S. Thesis, University of Pittsburgh, 2001.
13. Buxbaum, R.E.; Hsu, C.Z.; "Methods for Plating Palladium," U.S. Patent 5,149,429, Sept. 22, 1992 (1992).
14. Hsu, C.; Buxbaum, R.E.; "Electroless and Immersion Plating of Palladium on Zirconium," J. Electrochem. Soc. (1985) 132(10) 2419-2420.
15. Mardilovich, P.P.; She, Y.; Ma, Y.H.; Rei, M.-H.; "Defect-Free Palladium Membranes on Porous Stainless-Steel Support," AIChE Journal, 44 No. 2 (Feb. 1998) 310-322
16. Rothenberger, K.S.; Cugini, A.V.; Siriwardane, R.V.; Martello, D.V.; Poston, J.A.; Fisher, E.P.; Graham, W.J.; Balachandran, U.; Dorris, S.E.; "Performance Testing of Hydrogen Transport Membranes at Elevated Temperatures and Pressures." Am. Chem. Soc., Fuel Chem. Div., Prepr. Pap., Vol. 44 No. 4, (1999) 914-918.
17. Koffler, S.A.; Hudson, J.B.; Ansell, G.S.; "Hydrogen Permeation Through Alpha-Palladium," Transactions of the Metallurgical Society of AIME 245 (1969) 1735-1740.
18. Cantelli, R.; Mazzolai, F.; Nuovo, M.; 1971 J. Phys. (Paris), 32 C2-59.
19. Merisov, B.; Serdyuk, A.; Fal'ko, I.; Khadzhay, G.; Khotevitch, V.; Phys. Metals Metallogr. 32 (1971) 154.

20. DeGraff, L.; Rush, J., Livingston, R.; Flotow, H.; Rowe, J. 1 (1972) Jul-Ber. Jul-Conf., 6th, 301.
21. Volkl, J.; Alefeld, G.; Hydrogen Diffusion in Metals, in Diffusion in Solids, Recent Developments; Nowick, A.S. and Burton, J.J., eds. Academic Press, New York, NY, 1975, 232-295.
22. Steward, S.A.; "Review of Hydrogen Isotope Permeability Through Metals, Lawrence Livermore National Laboratory Report UCRL-53441, August 15, 1983.